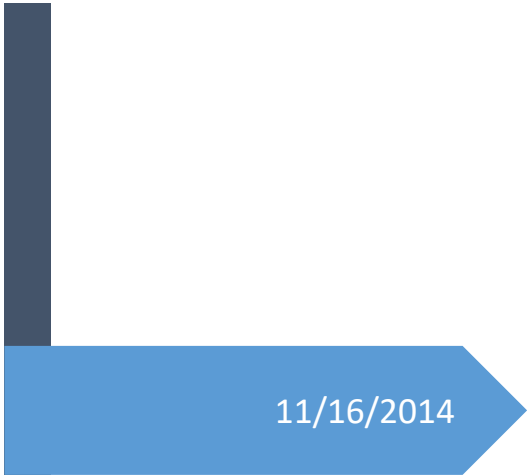
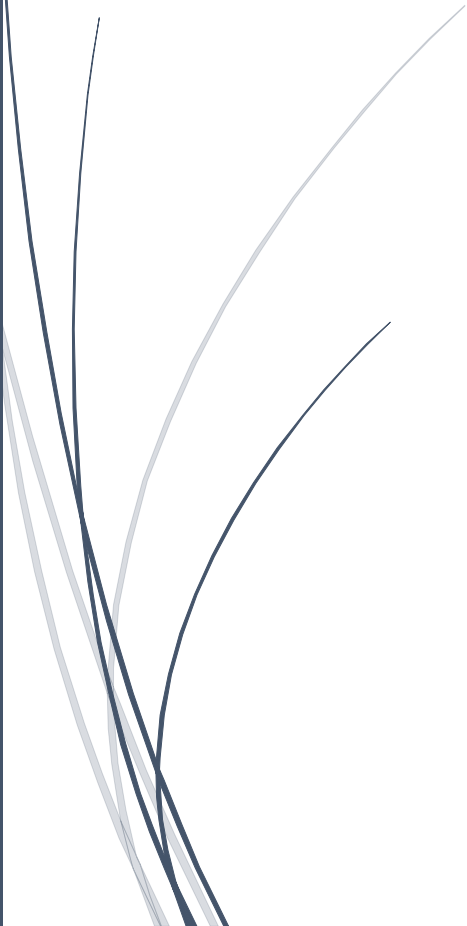


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11/16/2014

RSM Note Part 2

Extra Notes by Pratik Gautam

Several thin, curved lines in dark blue and light grey originate from the bottom left corner and sweep upwards and to the right.

This notebook belongs to Siddhant Rimal

Fundamental postulates of statistical mechanics

- ① Any Gas is composed of molecules, which are in motion and behave like very small elastic spheres.
- ② All the cells of phase space are of equal size.
- ③ All accessible microstate corresponding to the possible macrostate are Equally Probable. This is the fundamental postulate of statistical mechanics which is also called equal or priori probability.
- ④ The equilibrium state of a gas corresponds to the macrostate of maximum probability. (Equilibrium_{max})
- ⑤ The n. of molecules in the given system is constant as well as total energy is also constant.

(Q) State and prove Boltzmann theorem connecting entropy and thermodynamic probability

OR

Show that

$$S = k \log \Omega$$

where,

S = entropy

k = constant

Ω = thermodynamic probability.

Answer

Entropy and Probability

In 1896, Boltzmann discovered a relation between entropy (thermodynamic quantity) and probability (statistical quantity). He states that, "Equilibrium state of the system is the state of max probability" but thermodynamic point of view

equilibrium state of the system is the state of max entropy.

As entropy and thermodynamic probability have their maximum value in equilibrium state Boltzmann ~~and~~ concluded that entropy is function of thermodynamic probability.

ie. $S = f(\Omega) \quad \text{--- (1)}$

Let us consider two completely independent systems A and B having entropies S_1 and S_2 respectively. When molecules of A and B are mixed together then the entropy of molecules and the probability changes. Since entropy is additive quantity then the latter entropy will be given by

$$S = S_1 + S_2$$

where,

$$\left. \begin{aligned} S_1 &= f(\Omega_1) \\ S_2 &= f(\Omega_2) \end{aligned} \right\} \text{--- (2)}$$

S_1 is function of thermodynamic prob. of 1st.

~~Ag~~ Given

$\mathcal{N}_1$ = prob. of finding molecules of A.

$\mathcal{N}_2$ = " " " " " "

B.

Now,

prob. of finding both molecules at, with respect to given condition is,

$$\mathcal{N} = \mathcal{N}_1 \mathcal{N}_2 \quad \text{--- (3)}$$

Thus,

$$S = f(\mathcal{N}) = f(\mathcal{N}_1, \mathcal{N}_2)$$

$$\therefore S = f(\mathcal{N}_1) + f(\mathcal{N}_2)$$

$$f(\mathcal{N}_1, \mathcal{N}_2) = f(\mathcal{N}_1) + f(\mathcal{N}_2) \quad \text{--- (4)}$$

Diff partially eqn (4), w.r.t. $\mathcal{N}_1$ and $\mathcal{N}_2$ we get,

$$\mathcal{N}_2 f'(\mathcal{N}_1, \mathcal{N}_2) = f'(\mathcal{N}_1) \cdot \epsilon$$

$$\mathcal{N}_1 f'(\mathcal{N}_1, \mathcal{N}_2) = f'(\mathcal{N}_2)$$

Dividing,

$$\frac{\Omega_2}{\Omega_1} = \frac{f'(\Omega_1)}{f'(\Omega_2)}$$

$$\Rightarrow \Omega_2 f'(\Omega_2) = \Omega_1 f'(\Omega_1) = k$$

Thus,

~~f'~~

$$f'(\Omega_1) = \frac{k}{\Omega_1}$$

$$f'(\Omega_2) = \frac{k}{\Omega_2}$$

} — (5)

Integrating eqn (5), we get,

$$\int f'(\Omega_1) d\Omega_1 = \int \frac{k}{\Omega_1} d\Omega_1$$

$$f(\Omega_1) = k \log \Omega_1 + c_1 \text{ and}$$

$$\text{Similarly, } f(\Omega_2) = k \log \Omega_2 + c_2$$

In general,

$$f(n) = k \log n + c$$

$$\boxed{S = k \log n + c}$$

This is the required relation
between entropy and probability.
After applying boundary condition
constant quantity c vanishes
and we get,

$$\boxed{S = k \log n} \text{ which req. expn.}$$

Hence proved.

Boltzmann - Canonical distribution law

Let us consider $n_1, n_2, n_3, \dots, n_i$ be the number of molecules present in cell one, cell two $\dots$ cell i , in the thermodynamic equilibrium state. As the gas molecules are moving continuously n_i 's also change continuously in many different ways, but always maintain thermodynamic equilibrium, i.e. the state of maximum thermodynamic probability. Let

Let us suppose that n_i 's change obeying the fundamental postulates of statistical mechanics, i.e.

(1) Total n of molecules is constant.

$$N = n_1 + n_2 + \dots + n_i = \text{constant}$$

$$dN = dn_1 + dn_2 + \dots + dn_i = 0 \quad \text{--- (1)}$$

(2) Total energy of system is conserved.
constant.

$$W \propto E = \epsilon_1 n_1 + \epsilon_2 n_2 + \dots + \epsilon_i n_i = \text{constant.}$$

$$dE = \epsilon_1 dn_1 + \epsilon_2 dn_2 + \dots + \epsilon_i dn_i = 0 \quad \text{--- (2)}$$

(3) When gas is in equilibrium state the thermodynamic probability is maximum.

$$\text{ie. } d\Omega = 0$$

$$\Rightarrow d(\log \Omega) = 0 \quad \text{--- (3)}$$

We have,

$$\Omega = \frac{N!}{n_1! n_2! \dots n_i!}$$

taking log on both sides, we get,

$$\log(\Omega) = \log \left(\frac{N!}{n_1! n_2! \dots n_i!} \right) \quad \text{--- (4)}$$

$$\log(\Omega) = \log N! - \log n_1! - \log n_2! - \dots - \log n_i!$$

$$= \log N! - \log n_1! - \log n_2! - \dots - \log n_i!$$

$$\text{--- (5)}$$

Using Stirling's theorem

$$\text{(ie. } \log x! = x \log x - x \text{ for large no of } x)$$

We get

$$\log(u) = N \log N - N - [n_1 \log n_1 - n_1] - \dots - [n_i \log n_i - n_i]$$

$$\log(u) = N \log N - N - \left[\sum_i (n_i \log n_i - n_i) \right] \quad (4)$$

Diff. eqn (4) w.r.t $n_1, n_2, \dots, n_i$

$$d \log(u) = d \left[N \log N - N - \sum_i (n_i \log n_i - n_i) \right]$$

from eqn (3)

$$0 = 0 - \sum_i (n_i d \log n_i + \log n_i dn_i - dn_i)$$

$$\sum_i \left(n_i \frac{1}{n_i} dn_i + \log n_i dn_i - dn_i \right) = 0$$

$$\therefore \sum_i \log n_i dn_i = 0 \quad (5)$$

eqn (1) (2) & (5) are independent to each other. $\rightarrow$

$$\log n_1 dn_1 + \log n_2 dn_2 + \dots + \log n_i dn_i = 0$$

So we can combine them without loosing their independence. multiplying by arbitrary constants

Hence multiply eqn (i) by α and eqn (2) by β and adding the resulting equations with eqn (5) we get,

$$\alpha (\alpha d n_1 + \alpha d n_2 + \dots + \alpha d n_i) + \beta (\epsilon_1 d n_1 + \epsilon_2 d n_2 + \dots + \epsilon_i d n_i) + \log n_i d n_i = 0$$

$$\alpha (\alpha + \beta \epsilon_1 + \log n_i) d n_i + \dots + (\alpha + \beta \epsilon_i + \log n_i) d n_i = 0$$

Hence,

$$\alpha + \beta \epsilon_1 + \log n_i = 0$$

$$\alpha + \beta \epsilon_2 + \log n_2 = 0$$

In general,

$$\alpha + \beta \epsilon_i + \log n_i = 0$$

$$\text{or, } \log n_i = -(\alpha + \beta \epsilon_i)$$

$$\therefore n_i = e^{-\alpha} e^{-\beta \epsilon_i}$$

$$\therefore \boxed{n_i = A e^{-\beta \epsilon_i}} \text{ where } A = e^{-\alpha} = \text{constant.}$$

This equation gives the number of molecules in i^{th} cell ~~at~~ as a function of energy associated with each particle in that cell. And is called Boltzmann canonical distribution law.

Partition function

From Boltzmann canonical distn law, we have,

$$n_i = A e^{-\beta \epsilon_i}$$

where n_i is the num. of molecules in the i^{th} cell having energy ϵ_i in thermodynamical equil. state.

$$\therefore \sum n_i = A \sum e^{-\beta \epsilon_i} = N$$

Here, $\sum e^{-\beta \epsilon_i}$ is called partition function, which is represented by Z .

$$\therefore A \cdot Z = \sum e^{-\beta \epsilon_i}$$

$$\therefore A = \frac{N}{Z} = \frac{N}{\sum e^{-\beta \epsilon_i}}$$

Again,

$$\text{value of } \beta = \frac{1}{k_B T}$$

where, k_B = Boltzmann Constant
 T = absolute Temp.

Thus,

The n. of molecules in a cell having energy ϵ_i is given by,

$$n_i = A e^{-\frac{\epsilon_i}{k_B T}}$$

and the probability of energy

a molecule to have energy ϵ_i is given by,

$$P(\epsilon_i) = \frac{h_i}{N} = \frac{A}{N} e^{-\frac{\epsilon_i}{k_B T}}$$

$$= c e^{-\epsilon_i/k_B T} \text{ where } c = A/N = \text{constant}$$

We can find value of constant c by considering max prob.

$$\sum P(\epsilon_i) = 1$$

$$\therefore 1 = c \sum e^{-\epsilon_i/k_B T}$$

$$\therefore c = \frac{1}{\sum e^{-\epsilon_i/k_B T}}$$

Hence,

$$P(\epsilon_i) = \frac{e^{-\epsilon_i/k_B T}}{\sum e^{-\epsilon_i/k_B T}}$$

~~to find~~

(Q) Two states with energy difference $4.83 \times 10^{-21} \text{ J}$ occur with relative probability e^2 , calculate the temperature.
 $k_B = 1.38 \times 10^{-23} \text{ J/K}$

Soln

$$\Delta E = 4.83 \times 10^{-21} \text{ J} : E_1 - E_2 = 4.83 \times 10^{-21}$$

Also, $A = 1$

$$\frac{P_1}{P_2} = e^2$$

Now

$$\frac{e^{-E_1/k_B T}}{e^{-E_2/k_B T}} = e^2$$

$$e^{-(4.83 \times 10^{-21} + E_2)/k_B T} = e^{-E_2/k_B T} \cdot e$$

$$-(4.83 \times 10^{-21} + E_2)/k_B T = -E_2/k_B T + 1$$

$\Rightarrow$

$$-4.83 \times 10^{-21} / k_B T = e^{-2}$$

$$\Rightarrow \frac{-4.83 \times 10^{-21}}{1.38 \times 10^{-23} \times T} = -2$$

$$\Rightarrow T = 1.75 \times 10^2$$

$$\therefore T = 175 \text{ K}$$

(Tj)

Maxwell Boltzmann distribution law

(MB statistics)

Conditions of MB:

- 1) Any number of particle ($n=0, 1, 2, \dots$) so on can accommodated in same quantum state.
- 2) The particles are considered to be distinguishable.
- 3) The sum of particles in each quantum state is the total number of particles.
- 4) The sum of the energy of each

particle in the quantum state is the total energy.

Let us consider a system of 'N' of molecule of gas which are distinguishable. Suppose, n_1 of them have energy ϵ_1 , n_2 of them have energy ϵ_2 , n_i of them have energy ϵ_i .

Thus entire assembly of molecule can be divided into diff. states with energies $\epsilon_1, \epsilon_2, \dots, \epsilon_i$ with $n_1, n_2, \dots, n_i$ molecules.

(1) Total n. of molecule is constant

$$N = n_1 + n_2 + \dots + n_i = \text{constant.}$$

$$\delta N = \delta n_1 + \delta n_2 + \dots + \delta n_i = \text{constant} = 0 \quad \text{--- (1)}$$

(2) Total energy of system is constant

$$E = \epsilon_1 n_1 + \epsilon_2 n_2 + \dots + \epsilon_i n_i = \text{constant.}$$

~~(1)~~

$$V_i = n_i \geq 1$$

$$d\epsilon = \epsilon_1 dn_1 + \epsilon_2 dn_2 + \dots - \epsilon_i dn_i = 0 \quad (2)$$

Consider there are g_i cells with energy ϵ_i . Total num of ways in which n_i molecules can have energy ϵ_i is $(g_i)^{n_i}$. Hence, total num. of ways in which N molecules can be distributed among the various energy is,

$$W_i = g_1^{n_1} g_2^{n_2} \dots g_i^{n_i}$$

The number of ways in which groups of $n_1, n_2, \dots, n_i$ particles can be chosen from N particles is given by

$$W_2 = \frac{N!}{n_1! n_2! \dots n_i!}$$

The total num. of distg. ways in which N molecules can be distributed among the possible

$$\sum n_i = N$$

energy level is

(2)

$$\Omega = \omega_1 \omega_2$$

$$\Omega = N! \prod_i \frac{g_i^{n_i}}{n_i!}$$

$$\Omega = N! \prod_i \frac{g_i^{n_i}}{n_i!} \quad (3)$$

where Ω = thermodynamic prob.

taking log on both side of eqn (3).

$$\log \Omega = \log N! - \sum \log n_i! + \sum n_i \log g_i$$

(1)

Using ~~the~~ stirling approximation theorem,

$$\log \Omega = N \log N - N - \sum (n_i \log n_i - n_i) + \sum n_i \log g_i$$

(2)

$$\log \Omega = N \log N - \sum n_i \log n_i + \sum n_i \log g_i \quad (4)$$

Now, diff eqn (4) for maximum probability,
 $d \log n = 0$

and,

$$d \log n = - \sum_i n_i \frac{1}{n_i} dn_i - \sum_i \log n_i dn_i$$

$$- \sum_i \log g_i dn_i = 0$$

$$n \sum_i \log n_i dn_i - \sum_i \log g_i dn_i = 0$$

Multiply eqn (i) by α (ii) by β and
 to eqn (5).

$$\alpha \sum dn_i + \beta \sum \epsilon_i \epsilon n_i + \sum \log n_i dn_i - \sum \log g_i dn_i = 0$$

$$\Rightarrow \sum (\alpha + \beta \epsilon_i + \log n_i - \log g_i) dn_i = 0$$

$$\therefore \log \frac{n_i}{g_i} = -(\alpha + \beta \epsilon_i) \Rightarrow \boxed{n_i = g_i e^{-\alpha} e^{-\beta \epsilon_i}}$$

which is required eqn for M.B. statistics. It gives the number of particles ~~in~~ in its cell following Maxwell Boltzmann statistics.

Molecular Energys in ideal Gas

The M.B. distribution law is

$$n_i = g_i e^{-\alpha} e^{-\beta \epsilon_i}$$

The num. of molecules having energies betn E & $E + dE$ is

$$n(E) dE = \frac{2\pi N}{(\pi k_B T)^{3/2}} \sqrt{E} e^{-E/k_B T} dE$$

where,

N = tot. num of molecules

T = absolute temp.

k_B = Boltzmann constant

The total energy of system is

$$E = \int_0^{\infty} E n(E) dE$$

$$= \frac{2\pi N}{(\pi k_B T)^{3/2}} \int_0^{\infty} E^{3/2} e^{-E/k_B T} dE$$

$$= \frac{2\pi N}{(\pi k_B T)^{3/2}} \times \frac{3}{4} (k_B T)^2 \sqrt{\pi k_B T}$$

$$= \frac{3}{2} N k_B T$$

✓

The average energy of an ideal gas is

$$\frac{E}{N} = \frac{3}{2} k_B T$$

Maxwell Boltzmann Velocity Distribution.

We have,

$$n(E)dE = \frac{2\pi N}{(\pi k_B T)^{3/2}} \sqrt{E} e^{-E/k_B T} dE$$

$$\text{Put } E = \frac{1}{2} m v^2 \quad \therefore dE = m v dv$$

$$n(v)dv = \frac{\sqrt{2} N m^{3/2}}{(\pi k_B T)^{3/2}} v^2 e^{-\frac{mv^2}{2k_B T}} dv$$

This eqn represents num. of molecules with speed betw v and $v+dv$ in the assembly of ideal gas containing N num. of molecules at absolute temp T .

Bose-Einstein distribution law

(B.E statistics)

Conditions for B.E. statistics

1) Particles are identical and indistinguishable
example photons, helium atom at low temp. The particles are called Bosons. They have spin either 0 or integral.

2) Particles don't obey Pauli's Exclusion Principle. i.e. any num. of particles can accommodate in given quantum state.

3) The sum of energy of particles in the quantum state is equal to total energy.

(Q) Derive B.E. distn law.

Let us consider an assembly of N bosons. Let these particles be divided into quantum groups such that there are $n_1, n_2, \dots, n_i$ number of particles in group whose energies are $\epsilon_1, \epsilon_2, \dots, \epsilon_i$.

Let us consider that the box is divided into g_i sections by $(g_i - 1)$ partitions and n_i indistinguishable particles to be distributed among these sections. The permutation of n_i particles and $(g_i - 1)$ partitions are simultaneously given by, $n_i!$ and $(g_i - 1)!$ and combined permutation of $n_i!$ and $(g_i - 1)!$ is given by $(n_i + g_i - 1)!$. But this includes also the permutation among themselves and $(g_i - 1)$ among themselves, as these are internally indistinguishable. Hence, the actual ways in which n_i particles are to be distributed in g_i sublevels of i th section.

quantum state is

$$\frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!}$$

Similarly, various ways of distribution for other quantum state also can be obtained. Thus thermodynamic probability will be,

$$\Omega = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \quad \text{--- (1)}$$

as n_i and g_i are very large we can neglect 1.

$$\therefore \Omega = \prod_i \frac{(n_i + g_i)!}{n_i! g_i!} \quad \text{--- (2)}$$

Taking ~~log~~ log and ~~using~~ Stirling approximation.

$$\log \Omega = \sum_i \log(n_i + g_i)! - \log n_i! - \log g_i!$$

using Stirling approx.

$$\log N = \sum_i ((n_i + g_i) \log(n_i + g_i) - (n_i \log n_i - n_i) - (g_i \log g_i - g_i))$$

$$\log N = \sum_i ((n_i + g_i) \log(n_i + g_i) - n_i \log n_i - g_i \log g_i) \quad \text{--- (3)}$$

① n_i varies continuously but g_i is constant.

diff w.r.t n_i , we get

$$d \log N = \sum_i (\log(n_i + g_i) - \log n_i) dn_i = 0 \quad \text{--- (4)}$$

for maxm. prob.

$$d \log N = 0$$

$$\sum_i dn_i = 0 \quad \text{--- (5)}$$

$$\sum_i \epsilon_i dn_i = 0 \quad \text{--- (6)}$$

multi 5 by α and 6 by β and adding to 4 we get

$$\alpha dn_1 + \alpha dn_2 + \dots + \alpha dn_i + \beta \epsilon_i dn_1 + \beta \epsilon_i dn_2 + \dots + \beta \epsilon_i dn_i + \sum (\log(n_i + g_i) - \log n_i) dn_i = 0$$

$$\text{or } \left(\alpha + \beta \epsilon_i + \log \left(\frac{n_i + g_i}{n_i} \right) \right) dn_i = 0$$

$$\text{or } \log \left(\frac{n_i + g_i}{n_i} \right) = -(\alpha + \beta \epsilon_i)$$

$$\text{or } \frac{n_i + g_i}{n_i} = e^{-(\alpha + \beta \epsilon_i)}$$

$$\frac{g_i}{n_i} = e^{-(\alpha + \beta \epsilon_i)} - 1$$

$$\frac{n_i}{g_i} = \frac{1}{e^{(\alpha + \beta \epsilon_i)} - 1}$$

$$n_i = \frac{g_i}{e^{(\alpha + \beta \epsilon_i)} - 1} \quad \checkmark$$

Fermi-Dirac distribution law (F-D statistics)

Conditions

- 1) The sublevels consists only $n_i = 0$ or 1 i.e. The particles obey Pauli's Exclusion principle.
- 2) The particles are identical and indistinguishable. They have half spin. They are called fermions.
Ex: Electron, proton, neutron are called fermions.
- 3) The sum of energy possessed by a particle in each sublevel of diff. energy level is total energy.

$$\frac{g_i!}{n_i! (g_i - n_i)!}$$

$$\Omega = \prod \frac{g_i!}{n_i! (g_i - n_i)!}$$

$$\sum_i n_i = 0 \quad \text{--- (1)}$$

$$\sum_i n_i \epsilon_i = 0 \quad \text{--- (2)}$$

$$\int \log w = \sum_i \log n_i - \log (g_i - n_i) dn_i$$

$$0 = \sum_i \log n_i - \log (g_i - n_i) dn_i$$

$$\sum_i \left(\frac{\log n_i}{g_i - n_i} + \alpha + \beta \epsilon_i \right) dn_i = 0$$

$$\log \left(\frac{n_i}{g_i - n_i} \right) + \alpha + \beta \epsilon_i = 0$$

$$\frac{n_i}{g_i - n_i} = e^{-(\alpha + \beta \epsilon_i)}$$

$$n_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i} + 1}$$

Differences betⁿ three statistics

ie (MB, BE, FD)

MB

- Particles are distinguishable and only particles are taken into consideration.
- There is no restriction on the no. of particles in a given state.
- It is applicable to ideal gas molecules.
- The most probable distr. No is
$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta \epsilon_i}}$$

BE

- Particles are indistinguishable and only quantum states are taken into consideration.
- No restriction on the no. of particles in a given state.

- It is applicable to photons and symmetrical particles i.e. having spin 0 or integral (integer).
- The most probable distn No. is.

$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta \epsilon_i} - 1}$$

FD

- particles are indistinguishable and quantum states are taken into consideration.
- Only one particle may be in a given quantum state. i.e. particles follow Pauli's exclusion principle.
- It is applicable to electrons and elementary particles.
- The most probable distn is given by

$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta \epsilon_i} + 1}$$

If $e \gg k_B T$, BE distr FD distr
ends to MB distr.

Electron Gas

$$E_F = \frac{h^2}{2m} \left(\frac{3n}{8\pi V} \right)^{2/3}$$

$$E_F = \frac{h^2}{8m} \left(\frac{3n}{\pi V} \right)^{2/3}$$

Fermi temperature:

$$T_F = \frac{E_F}{k_B}$$

(Q) The n. of electrons per unit Vol^m
available for conduction in sodium
metal is 2.5×10^{28} electrons/ m^3 .
Calculate the Fermi energy and
Fermi temp.

Soln:

$m = \text{mass of electron} =$

$$\frac{m}{v} = 2.5 \times 10^{28} \quad 63.5$$

$\frac{m}{v}$

$$h = \frac{3MA}{A}$$

$$= \frac{3.55 \times 6.23 \times 10^{23}}{63.5}$$

$$E_f = \frac{h^2}{2m} \cdot \left(\frac{3n}{8a} \right)^2$$

$$E_f = 3.65 \times 10^{-15} \text{ eV}$$

①

Crystal structure

Bonding

① Vander Waals force: (Weak force)

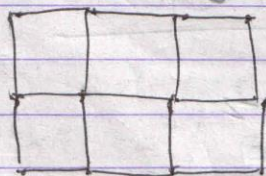
② Metallic bonding

③ Crystalline

④ amorphous

Crystal:

A ~~sto~~ solid having definite set with its atoms, ions or molecules arranged in some regular repetition in 3D pattern is called crystal. In a crystalline solid atoms are regularly arranged in periodic arrangement of atoms in a crystal is called lattice.
(arrangement)



Basis:

The structure of all the crystal in terms of a lattice with a group of atoms attached to each lattice point. The group of atom is a basis.

Unit cell:

It is defined as the volume of solid

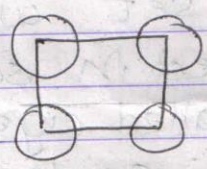
$$a = \sqrt{L^2 + K^2 + I^2} \quad \text{--- (2) //}$$

②

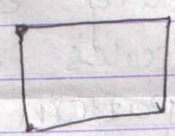
from which entire crystal can be constructed by the ~~translati~~ translational repetition in 3D.

Primitive Cell

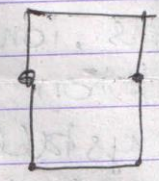
A type of Unit cell which contains only one lattice point or only one atom at the ~~corn~~ corners only and minimum volume cell is called primitive cell.



a) primitive

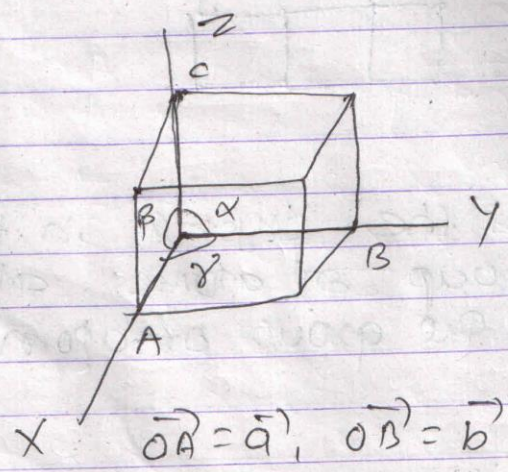


b) primitive



c) Non-primitive.

Lattice parameter



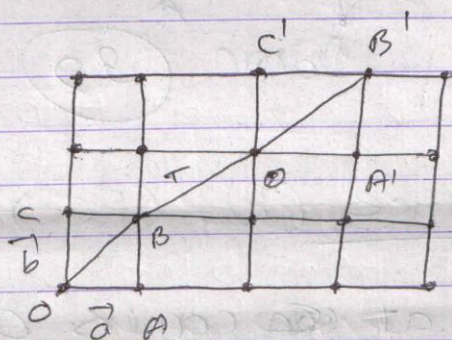
$$\vec{OA} = \vec{a}, \vec{OB} = \vec{b}, \vec{OC} = \vec{c}$$

(3)

Here, vector $\vec{a}$, $\vec{b}$, $\vec{c}$ are three primitive parameters and α , β , γ are three interfacial angles. These a , b , c , and α , β , γ are called lattice parameters.

Vol^m of primitive cell $(V) = (\vec{a} \times \vec{b}) \cdot \vec{c}$.

Crystal translation vector.



$$\vec{T} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$$

where n_1, n_2, n_3 are arbitrary integer.
 T is called lattice / crystal vector.

Bravais lattice

The group of four types of symmetry operation at a point is called point group. These point groups form the basis for the construction of different types of ~~the~~ lattice called ~~the~~ Bravais lattice. The possible Bravais lattice are:

Bravais

$$a = \sqrt{h^2 + k^2 + l^2} \quad \text{--- (2) //$$

(Simple cubic)
(SC)



④
Total of 8 atoms

1) Primitive lattice (P):

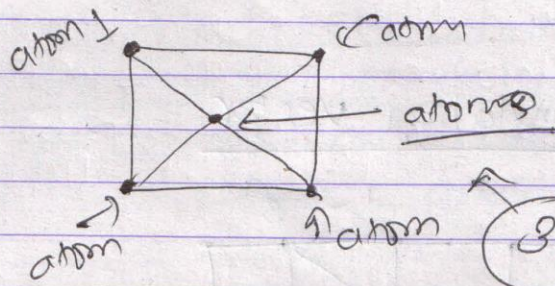
→ Lattice points are situated only at corners of unit cell. $r = \frac{a}{2}$ $N = 1$ $P = 52\%$

2) Body centered lattice (I) (BCC)

→ Lattice points are at corners and also at the intersection of the largest diagonal of the unit cell.

$$r = \frac{\sqrt{3}a}{4}$$

$$N = 2$$



Total of 2 atoms

(3D)

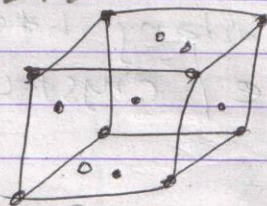
packing fraction = 67%

3) Face centered lattice (F) (FCC)

→ Lattice points are at ~~corners~~ corners and at the center of each face of unit cell.

$$r = \frac{a}{2\sqrt{2}}$$

$$N = 4$$



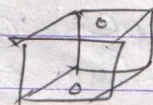
← atoms at faces

④ Total of 4

packing fraction = 74%

4) Base centered (C)

Lattice points are at corners and at the center of two faces of unit cell ~~are~~ are opp. to each other.



→ total 2 atoms

(5)

N. of atom within a primitive

$$N = N_i + \frac{N_c}{8} + \frac{N_f}{2} ; \begin{array}{l} N_c = \text{n. of atoms in corners,} \\ N_f = \text{n. of atoms in faces,} \\ N_i = \text{atom inside.} \end{array}$$

System of Crystal structure

	Bravais		
Cubic	PIF	$a=b=c$	$\alpha=\beta=\gamma=90^\circ$
Tetragonal	PI	$a=b \neq c$	$\alpha=\beta=\gamma=90^\circ$
Orthorhombic	PIFC	$a \neq b \neq c$	$\alpha=\beta=\gamma=90^\circ$
Hexagonal	P	$a \neq b \neq c$	$\alpha=\beta=90^\circ, \gamma=120^\circ$
Rhombohedral	P	$a=b=c$	$\alpha=\beta=\gamma \neq 90^\circ$
Monoclinic	P, C	$a \neq b \neq c$	$\alpha=\gamma=90^\circ, \beta \neq 90^\circ$

~~Triclinic~~

Triclinic	P	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$
-----------	---	-------------------	---

Packing Fraction

$$P = \frac{\text{vol}^m \text{ of atom in unit cell}}{\text{vol}^m \text{ of unit cell}}$$

It is the ratio of vol^m of atoms in ~~the~~ a unit cell to the vol^m of unit cell. It gives idea about closeness of atom.

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{--- (2) //}$$

1) Primitive lattice (P):

(Simple cubic)
(SC)



④
total of 8 atoms

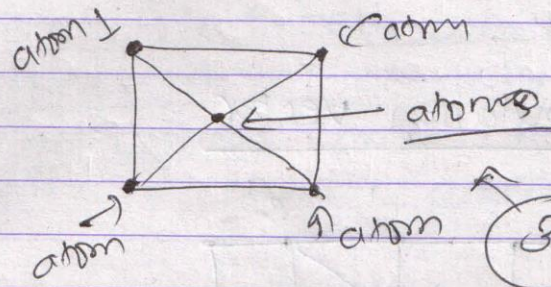
→ Lattice points are situated only at corners of unit cell. $r = \frac{a}{2}$ $N = 1$ $P = 52\%$

2) Body centered lattice (I) (BCC)

→ Lattice points are at corners and also at the intersection of the largest diagonal of the unit cell.

$r = \frac{\sqrt{3}a}{4}$

$N = 2$



total of 2 atoms

(3D)

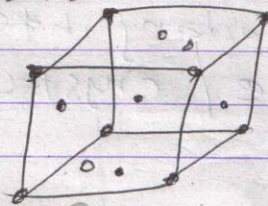
✓ packing fraction = 67%

3) Face centered lattice (F) (FCC)

→ Lattice points are at ~~corners~~ corners and at the center of each face of unit cell.

$r = \frac{a}{2\sqrt{2}}$

$N = 4$



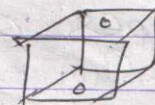
← atoms at faces

total of 4

packing fraction = 74%

4) Base centered. (C)

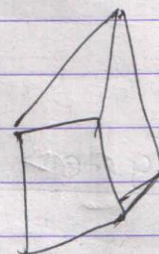
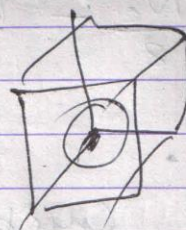
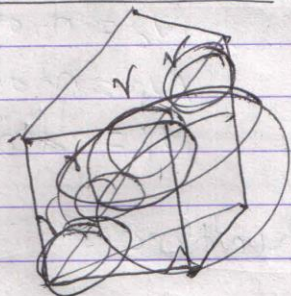
→ Lattice points are at corners and at the center of two faces of unit cell ~~are~~ are opp. to each other.



→ total 2 atoms,

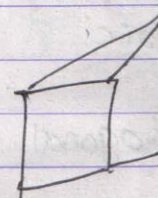
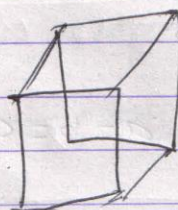
⑥

Atomic Radius:



BCC: $\frac{\sqrt{3}a}{4}$ FCC: $r = \frac{a}{2\sqrt{2}}$

SC: $a/2$



Co-ordination Number

The num. of nearest neighbouring atom than an atom has in the unit cell is called co-ordination number.

For simple cubic co-ordination Number is

8. Body centered co-ordination Number is, 8.

Face centered is four.

Proof

Find packing fraction of simple cubic.

we have

$$N = \frac{N_i}{1} + \frac{N_c}{8} + \frac{N_f}{2}$$

$$N = \frac{8}{8}$$

$$\therefore N = 1$$

In simple cubic structure n. of atom within the cell is one.

Atomic radius of simple cubic is $r = \frac{a}{2}$.

(8)

(7)

Vol^m of atom is $\frac{4}{3} \pi r^3$ in a cell

$$= \frac{4}{3} \pi \frac{a^3}{8}$$

Vol^m of unit cell = a^3

∴ Now

$$P = \frac{\frac{4}{3} \pi \frac{a^3}{8}}{a^3}$$

$$= \frac{2\pi}{6}$$

$$P = \frac{\frac{4}{3} \pi \frac{a^3}{8}}{a^3}$$

$$= \frac{\pi}{6}$$

$$= 52\%$$

~~$P = \frac{\pi}{6} = 52\%$~~

find packing fraction for BCC.

$$r = \frac{\sqrt{3}a}{4}$$

Vol^m of unit cell = a^3

Vol^m of atom in a cell =

$$\frac{4}{3} \pi \left(\frac{\sqrt{3}a}{4} \right)^3$$

$$N_0 = N_i + N_c + N_f$$

$$= 1 + 8 \times \frac{1}{8} = 2$$

$$a = \frac{\sqrt{h^2 + k^2 + l^2}}{2} //$$

~~$P =$~~

$$P = \frac{a^3}{2 \times \frac{4}{3} \pi \left(\frac{\sqrt{3}a}{4} \right)^3}$$

$$P = 67\%$$

(8)

Packing fraction for FCC

$$N = 4$$

$$P = \frac{\text{Vol of } N \text{ atoms in unit cells}}{N \times \text{Vol of atom in cell}}$$

$$P = \frac{a^3}{4 \times \frac{4}{3} \pi \left(\frac{a}{2\sqrt{2}} \right)^3}$$

$$\Rightarrow P = 74\%$$

If a lattice parameter of fcc crystal is $2.14 \text{ \AA}$, find the radius of particle.

for FCC,

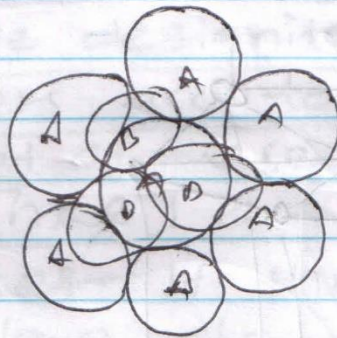
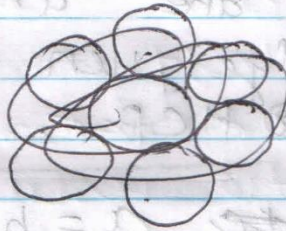
$$r = \frac{a}{2\sqrt{2}}$$

$$\therefore r = \frac{2.14 \times 10^{-10}}{2\sqrt{2}}$$

$$\therefore r =$$

mp

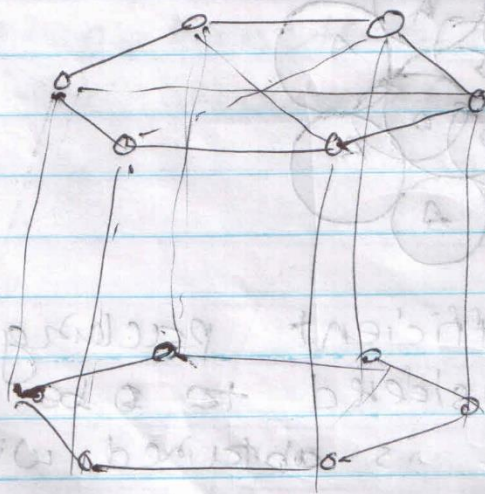
Hexagonal closed packed structure (HCP).



The most efficient packing of atoms, considered to be so in a plane is obtained with each atom (A) touching six atoms in a plane. Second similar layer can be added by placing atoms (B) in contact with three atoms. Third

layer of atoms can be arranged in 2 ways. If 'C's are arranged in space which are not occupied by B. Then the structure is FCC. But if C's are arranged just above the edge, then the structure is called ~~the~~ HCP.

In HCP, ~~$a \neq b \neq c$~~ $a = b \neq c$, $c = 1.66$
 $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$.



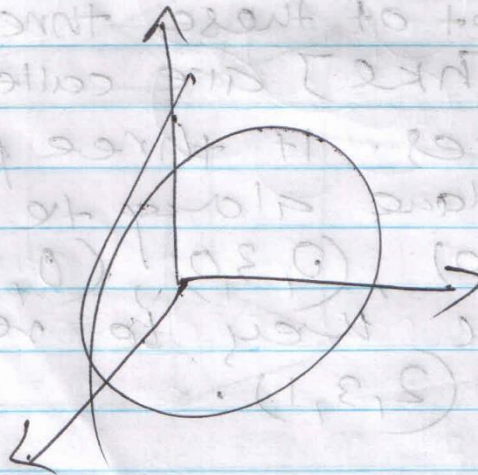
The co-ordination num. of HCP is 12. The n. of atoms per unit cell is 4. The packing factor is 74% equal to FCC.

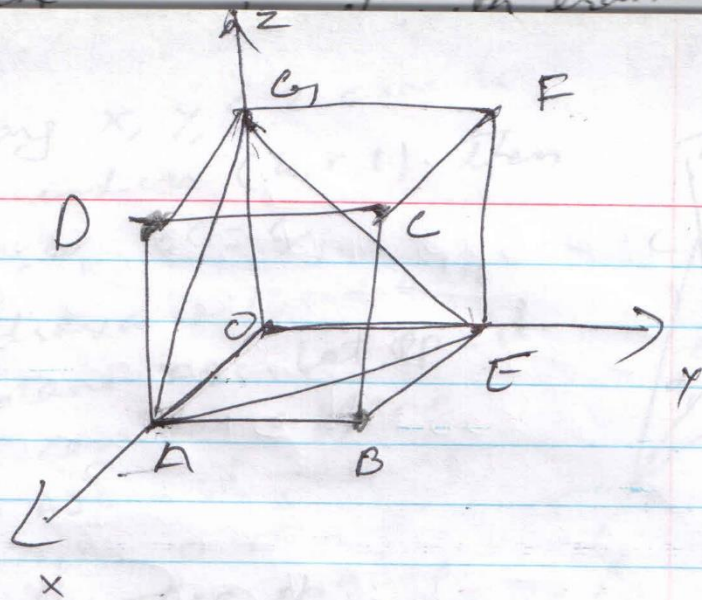
Miller indices $[hkl]$

A two dimensional lattice is called lattice plane each lattice plane can be designated by three integers acc. to scientific miller. A set of these three numbers ~~the~~ $[hkl]$ are called miller indices. If three points of the plane along the axes are $(2, 0, 0)$, $(0, 3, 0)$, $(0, 0, 1)$. The plane may be represented by $(2, 3, 1)$.

Rules to find Miller indices

- (1) Find the intercepts ~~find~~ formed by a plane on the crystal axes $\vec{a}, \vec{b}, \vec{c}$.
- (2) Find the multiplier of axes.
- (3) take the reciprocal of these multiplier and then reduce to the smallest three integers having same ratio.
- (4) Denoted the result in $[hkl]$ enclosed in parenthesis.
- If intercept are negative, put bar for example $eq [\bar{h}, k, l]$ for the plane





For the plane ABCD
intercepts a, ∞, ∞

Multipiers $1, \infty, \infty$

reciprocal $\frac{1}{1}, \frac{1}{\infty}, \frac{1}{\infty}$
 $(1, 0, 0)$

For plane AGE,
intercepts a, g, e

Multipiers $1, 1, 1$

reciprocal $\frac{1}{1}, \frac{1}{1}, \frac{1}{1}$
 $(1, 1, 1)$

(8)

lattice spacing

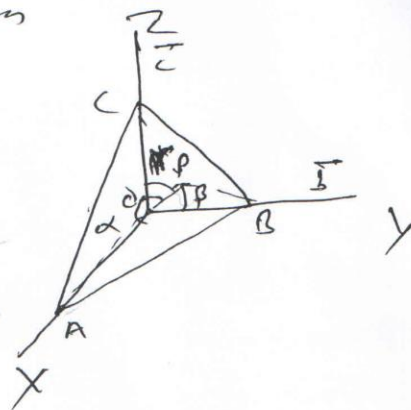
The perpendicular distance betⁿ two lattice planes represented by same Miller indices is called lattice spacing.

Consider a unit cell with translation vectors $\vec{a}, \vec{b}, \vec{c}$ along x, y, z axes resp. Let ABC be a plane with Miller indices (h, k, l) . Then

$$OA = \frac{a}{h}, OB = \frac{b}{k}, OC = \frac{c}{l}$$

Now draw a perpendicular OP on the plane ABC. Let $OP = d$.

If we consider a plane parallel to ABC and passing through origin O then 'd' gives the lattice spacing of planes with Miller indices (h, k, l)



joining OA, OB & OC, α, β & γ are direction cosines then in $\triangle OBP$

$$\cos \beta = \frac{OP}{OB} = \frac{d}{b/k} = \frac{dk}{b}$$

$$\text{Similarly } \cos \alpha = \frac{dh}{a}, \cos \gamma = \frac{dl}{c}$$

we know $\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$

$$\Rightarrow \frac{d^2 h^2}{a^2} + \frac{d^2 k^2}{b^2} + \frac{d^2 l^2}{c^2} = 1$$

$$d^2 = \frac{1}{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)}$$

$$\therefore d = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}} \quad \text{--- (1)}$$

this is the expⁿ of lattice spacing for cubic crystal $a=b=c$

$$\therefore d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{--- (2) //}$$

This is the expression of lattice spacing for cubic crystal; $a=b=c$

$$\therefore d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2)$$

A crystal can be defined by using set of translation vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$ where each lattice point is given by $\vec{r} = m\vec{a} + n\vec{b} + p\vec{c}$ where m, n and p are integers.

There exists another set of vectors $\vec{A}$, $\vec{B}$, $\vec{C}$ which are called reciprocals of $\vec{a}$, $\vec{b}$, $\vec{c}$ and this defines a crystal structure. These vectors are called reciprocal vectors and the defined crystal is called reciprocal crystal. Mathematically,

$$\left. \begin{aligned} \vec{A} &= 2\pi \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot (\vec{b} \times \vec{c})} \\ \vec{B} &= 2\pi \frac{\vec{c} \times \vec{a}}{\vec{b} \cdot (\vec{c} \times \vec{a})} \\ \vec{C} &= 2\pi \frac{\vec{a} \times \vec{b}}{\vec{c} \cdot (\vec{a} \times \vec{b})} \end{aligned} \right\} \quad (2)$$

Direct lattice; $\vec{a}$, $\vec{b}$, $\vec{c}$

From eqn (2),

$$\left. \begin{aligned} \vec{a} \cdot \vec{A} &= 2\pi & \vec{a} \cdot \vec{B} &= 0 & \vec{a} \cdot \vec{C} &= 0 \\ \vec{b} \cdot \vec{B} &= 2\pi & \vec{b} \cdot \vec{A} &= 0 & \vec{b} \cdot \vec{C} &= 0 \\ \vec{c} \cdot \vec{C} &= 2\pi & \vec{c} \cdot \vec{A} &= 0 & \vec{c} \cdot \vec{B} &= 0 \end{aligned} \right\} \quad (3)$$

These properties show that $\vec{a}$ is reciprocal of $\vec{A}$ and perpendicular to $\vec{B}$ and $\vec{C}$.

Similarly,

$\vec{b}$ is reciprocal of $\vec{B}$ and $\vec{c}$ is of $\vec{C}$.

Now, each lattice point of reciprocal lattices is given by

~~Q3~~

$$\vec{G} = h\vec{A} + k\vec{B} + l\vec{C}$$

where h, k, l are integers

VOLUME OF UNIT CELL OF RECIPROCAL LATTICE / VECTOR

$$V' = \vec{a} \cdot (\vec{b} \times \vec{c})$$

$$V = \vec{A} \cdot (\vec{B} \times \vec{C})$$

Let $\vec{a}, \vec{b}, \vec{c}$ and $\vec{A}, \vec{B}, \vec{C}$ are two primitive translation vectors and reciprocal lattice vectors respectively. The volume of unit cell of reciprocal lattice is given by

$$\vec{A} \cdot (\vec{B} \times \vec{C})$$

Now,

$$\vec{B} \times \vec{C} = \vec{B} \times \frac{2\pi (\vec{A} \times \vec{B})}{\vec{A} \cdot (\vec{B} \times \vec{C})}$$

$$= \frac{2\pi}{\vec{A} \cdot (\vec{B} \times \vec{C})} \vec{B} \times (\vec{A} \times \vec{B})$$

$$= \frac{2\pi}{\vec{A} \cdot (\vec{B} \times \vec{C})} [\vec{A}(\vec{B} \cdot \vec{B}) - \vec{B}(\vec{B} \cdot \vec{A})]$$

$$= \frac{4\pi^2 \vec{A}}{\vec{A} \cdot (\vec{B} \times \vec{C})}$$

Then,

$$\vec{A} \cdot (\vec{B} \times \vec{C}) = \frac{4\pi^2 \vec{A} \cdot \vec{A}}{\vec{A} \cdot (\vec{B} \times \vec{C})}$$

$$\therefore V = \frac{(2\pi)^3}{V'}$$

where V is volume of unit cell of reciprocal vectors
 V' is volume of unit cell of primitive/lattice vectors.

RECIPROCAL LATTICE OF S.C LATTICE

Let the primitive translation vectors of simple cubic cell be $\vec{a}, \vec{b}, \vec{c}$. Then we can write

$$\vec{a} = a \hat{x}$$

$$\vec{b} = a \hat{y}$$

$$\vec{c} = a \hat{z}$$

along $\hat{x}, \hat{y}, \hat{z}$ directions.

~~Along~~

Find the volume of direct cell of primitive lattice.

The volume of cubic cell of direct lattice is

$$\begin{aligned} V &= \vec{a} \cdot (\vec{b} \times \vec{c}) = \\ &= a \hat{x} \cdot a^2 \hat{x} \\ &= a^3 \end{aligned}$$

$$\begin{array}{l} \vec{A} \cdot \vec{B} = AB \cos \theta \\ \hat{i} \cdot \hat{i} = 1 \\ A \times B = AB \\ a \hat{y} \times a \hat{z} = a^2 \hat{x} \end{array}$$

Similarly,

$$\vec{B} = \frac{2\pi\hat{y}}{a}$$

$$\vec{C} = \frac{2\pi\hat{z}}{a}$$

RECIPROCAL LATTICE FOR ~~SIMPLE~~ BODY-CENTRED CUBIC

$$\vec{a} = \frac{a}{2} (\hat{x} + \hat{y} - \hat{z})$$

$$\vec{b} = \frac{a}{2} (-\hat{x} + \hat{y} + \hat{z})$$

$$\vec{c} = \frac{a}{2} (\hat{x} - \hat{y} + \hat{z})$$

Volume of BCC of direct lattice is

$$V = \vec{a} \cdot (\vec{b} \times \vec{c})$$

$$= \frac{\vec{a} \cdot a^2}{4} \cancel{(\hat{x} + \hat{y} + \hat{z})} (\hat{x} + \hat{y} - \hat{z}) \times (-\hat{x} + \hat{y} + \hat{z})$$

$$= \frac{\vec{a} \cdot a^2}{4}$$

$$\begin{vmatrix} i & j & k \\ x & y & -z \\ -x & y & z \end{vmatrix}$$

$$2yz\hat{i} - 0 + 2xy\hat{k}$$

$$= \vec{a} \frac{a^2}{4} (\hat{z} + \hat{y} - \hat{z} + \hat{x} + \hat{y} + \hat{x})$$

$$= \vec{a} \cdot \frac{a^2}{2} (\hat{x} + \hat{y})$$

$$= \frac{a^3}{4} (\hat{x} + \hat{y} - \hat{z}) (\hat{x} + \hat{y})$$

$$V = \frac{a^3}{4} (1+1)$$

$$= \frac{a^3}{2}$$

$$\vec{A} = \frac{2\pi}{\vec{c}} \vec{b} \times \vec{c}$$

$$\vec{c} (\vec{b} \times \vec{c})$$

$$= \frac{2\pi a^2 (\hat{x} + \hat{y})}{\frac{a^3}{2}}$$

$$=$$